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16. ABSTRACT

This report describes the field efforts over two snow seasons in central Pennsylvania. Due to a prolonged drought for the past two years, only a limited number of snow/rain events were sampled. The authors are careful to limit the conclusions to the specific site under study. However, the dynamics of the situation are such that conditions found at the central Pennsylvania site are typical for many of the sites in the wet deposition network.

The goal of the project was to determine if snow chemistry from samples collected in the Aerochem Metrics sampler (used in the NADP/NTN Network) was representative of the entire event or was it biased due to field sampling difficulties. To evaluate this question, the investigators set up three wet deposition samplers; one that operated in the normal manner (sensor operated), one that operated in the normal manner except that it was manually activated at the start and end of an event, and one that had the collection buckets changed three times during an event. Three precipitation volume collection gauges were also located at the site; one regular gauge, one gauge that had an Alter sheild attached, and one that had a Nipher shield attached. Meteorology instrumentation was also installed.

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INTRODUCTION

The National Atmospheric Deposition Program (NADP) and the National Trends Network (NTN) utilize Aerochem Metrics wet/dry samplers to collect precipitation for chemical analysis. This instrument consists of a two-container system with a movable lid that is designed to expose a wet-side container and cover a dry-side container during periods of precipitation, and vice versa. A sensor mounted on the instrument reacts electrically to the onset of precipitation causing the lid to move. Heaters mounted below the sensor serve to both melt snow and ice as well as evaporate moisture from the sensor. This instrument is used at all NADP and NTN monitoring sites and is used to sample both liquid and solid forms of precipitation. The standard sampling period is one week.

Co-located with each Aerochem Metrics precipitation sampler is an unshielded Belfort weighing-type recording rain gauge. Each rain gauge is equipped with a timer/chart recorder keyed to the sampling interval of one week and an event recorder. The weekly interpretation of the rain gauge chart by site operators provides daily and weekly amounts of precipitation. The coincidence of Aerochem Metrics collector operation with precipitation events is determined through the tracing of the event recorder. The volume of weekly precipitation from the rain gauge should correspond to the volume of liquid present in the wet-side container of the Aerochem Metrics collector. Precipitation measurements from the Belfort rain gauge are used in all calculations of wet deposition and in determining precipitation-weighted mean annual and seasonal concentrations of solutes found in precipitation.

Calculations of wet depositions and precipitation-weighted mean concentrations are influenced by the accuracy of precipitation measurements and the catch efficiency of the Aerochem Metrics collector. Errors in precipitation measurements can be attributed to instrumental and operational/observational problems, as well as errors associated with siting and climatic fluctuations. Instrumental errors include the inability of the rain gauge to record small precipitation events (response time), damage to the rain gauge orifice, and problems associated with the clock drive mechanism. Operational/observational problems include mistakes in interpreting the rain gauge chart and errors resulting from improper calibration of the weighing mechanism. Siting and climatic problems include: evaporation, splash, adhesion, geometry of gauge, form of precipitation, and wind speed.

In general, the greatest single source of error in precipitation measurements is associated with wind. The effects of wind are due primarily to an increase in pressure on the windward side of the gauge, a decrease in pressure and a marked acceleration of wind over the gauge orifice and the formation of eddy currents over and within the gauge orifice. In general, precipitation measurement errors increase as wind velocity increases, are

greatest for light versus heavy rainfall, and are greatest for snow versus rain, particularly light, dry snow. Another potential source of error in obtaining accurate precipitation measurements is associated with gauge response time and mistakes in interpreting the rain gauge chart. The frequency of these errors is greatest for light intensity precipitation events, particularly snowfall.

Inaccuracies in precipitation measurements associated with wind can be reduced by installing a wind shield around the rain gauge. Such shields are designed to divert the flow of air down and around the rain gauge and to eliminate updrafts. There are basically two types of shields. The Alter shield is a ring approximately six feet in diameter that is placed around the gauge from which hangs swinging metal slats. The shield extends one-half inch above the rain gauge orifice. The Nipher shield is a rigid, inverted bell-shaped solid device constructed of fiberglas and made specifically for the Belfort rain gauge. The device consists of a 28-inch cylinder that is used to extend 20 inches vertically the 8-inch orifice of the Belfort gauge. The inverted bell-shaped device is attached to the housing of the Belfort gauge and positioned at the same height as the extension from the rain gauge orifice. Comparisons of the Alter and Nipher shields have shown that the Nipher shield is superior to the Alter shield, especially when precipitation falls as snow.

A slow response of the Aerochem Metrics collector to the onset of precipitation or the frequent opening and closing of the movable roof during low intensity storms can result in a loss of precipitation from which solute concentrations are determined. This loss in turn can result in an over- or under-estimation of the solute concentrations, depending upon the temporal variability of solute concentrations during a storm and the relative solute concentrations of sampled and unsampled precipitation. The response time of the Aerochem Metrics varies with the form of precipitation and appears to be longer for light, dry snow than for low intensity rainfall.

Another problem associated with the Aerochem Metrics precipitation collector is its aerodynamics and the effect wind might have on the collector's ability to capture precipitation. In the above discussion, it was pointed out that the catch efficiency of the Belfort rain gauge is affected by wind and that better estimates of the true depth of precipitation can be obtained using wind shields around the rain gauge. The same wind-related problems apply to the Aerochem Metrics collector. These problems may be even more severe given the shape and aerodynamics of the sampler. Consequently, the depth of precipitation caught in the wet-side container may be considerably less than the actual depth of precipitation. In fact, comparison of wet-side bucket volumes with unshielded rain gauge measurements at four NADP/NTN sites in Pennsylvania in 1987 demonstrates these problems. The ratio of bucket volume to rain gauge volume ranged from 0.91 to 0.98 during the warm season and from 0.68 to 0.94 during the cold period at the four sites. The

lower ratios during the cold period reflect difficulties associated with sampling snow. The lowest cold period ratio was associated with the site that received the largest percentage of its annual precipitation as snowfall.

Recognizing potential problems and limitations of Aerochem Metrics samplers and unshielded Belfort rain gauges and realizing that these problems might affect wet deposition estimates and the calculation of precipitation-weighted mean concentrations from the NADP/NTN, a study was undertaken to compare cold season precipitation measurements from unshielded and Nipher- and Alter-shielded rain gauges located in an area subject to high wind speeds. These precipitation measurements were compared to volume measurements from sensor-activated and manually-activated Aerochem Metrics collectors. The chemical concentrations found in these composite samples were compared to precipitation-weighted mean concentrations obtained from sequential samples collected from an Aerochem Metrics sampler. The sensor-activated, manually collected sequential samples were evaluated to determine temporal variability in solute concentrations during winter storms and how this variability might affect deposition estimates. Differences in precipitation estimates from shielded and unshielded rain gauges were evaluated to determine what impact these differences might have on total estimates of wet deposition during selected precipitation events.

SITE LOCATION AND DESCRIPTION

This study was conducted at the University Park campus of The Pennsylvania State University located in the southern portion of Centre County near State College, Pennsylvania. Instruments were installed within the oval of the University's outdoor Running Track located at latitude 40 48' North and longitude 77 51' West. This site was selected because it is level and subject to windy conditions due to a long, open fetch upwind of the track. Although the site was located on the Penn State Campus, storms approaching the research site were not affected directly by neighboring buildings and vegetation. The track is located in the center of a wide east-west oriented valley within the Ridge and Valley Province of central Pennsylvania.

INSTRUMENTATION AND INSTALLATION

Equipment used in this study consisted of three Aerochem Metrics wet/dry precipitation collectors (Model 301), three Belfort weighing bucket-type recording rain gauges, an Alter wind shield, a Nipher wind shield, and a R.M. Young wind run anemometer (Model #6106) with wind direction capabilities (Model #6301). The Nipher shield was specifically designed for the Belfort gauge and

purchased from the Canadian Meteorological Service. During the winter of 1988, only two Belfort recording gauges were utilized as the Nipher shield was not received until April, 1988.

Two adjacent Aerochem Metrics precipitation collectors were hooked-up to a common precipitation sensor. One of the samplers was used to collect sequential samples that were manually removed from the samplers. The other sampler remained exposed to precipitation during the entire storm. This composite, event sample was removed for chemical analysis immediately after cessation of precipitation. Essentially, this sampler functioned the same as samplers located at NADP/NTN monitoring sites, although it was operated on an event basis instead of the normal weekly sampling interval.

A third Aerochem Metrics sampler was also installed at the site to obtain another composite event sample. Unlike the sensor activated samplers, this sampler was manually opened at the beginning of a storm and remained open during the entire storm. Since this sampler was not activated by a sensor and thus not subject to periodic opening and closing of the lid, a problem that is frequently encountered at NADP/NTN sites, its sample volume and chemistry was considered to be representative of the entire event. However, it should be noted that samples from the manually-operated sampler might also contain dry deposition that may have fallen in the sample container during intervals when precipitation temporarily ceased. During such temporary interruptions, sensor-activated samplers would (should) cover the wet-side bucket to protect against dryfall inputs into the wet-only sample. The manually-operated composite sample was removed for analyses immediately upon cessation of precipitation.

During the winter of 1988, two Belfort weighing-type rain gauges were installed at the site to measure precipitation. Both gauges were equipped with event recorders. The event recorder and rain gauge pen traces provided a record of precipitation and the coincidence of operation of the Aerochem Metrics samplers that were activated by the precipitation sensor. One of the rain gauges was equipped with an Alter-type wind shield; the other was exposed directly to prevailing winds. In 1989, an additional Belfort rain gauge was installed at the site. This gauge was equipped with a Nipher-type wind shield. Prior to installation, each rain gauge was calibrated following procedures recommended by the manufacturer.

Co-located with the above equipment was a R. M. Young wind run anemometer (Model #6106) with wind vane (Model #6301). These instruments were installed to provide a measure of wind direction and speed to aid in the interpretation of the results.

All instruments were positioned along a north-south transit with each piece of equipment being approximately 12 to 15 feet from the nearest instrument. The wet-side container of the Aerochem Metrics samplers were oriented to the west per NADP/NTN installation protocols. The recording rain gauges and wind

shields were installed according to manufacturer specifications. The Aerochem Metric samplers were operated with alternating current. The anemometer was powered by a 12-volt battery.

SAMPLING PROCEDURES

Prior to each storm, clean buckets were placed in the Aerochem Metrics collectors. Upon initiation of precipitation, the manually-operated collector was opened and left open during the entire storm. Essentially, analyses from this sample were used to describe the true chemical composition of each event sampled. The other collectors were activated by a standard precipitation sensor mounted on one of the samplers.

Precipitation samples from one of the sensor-activated collectors were collected sequentially. An attempt was made to collect three samples per storm with sufficient volume to permit complete chemical analysis. Essentially these samples were to represent the chemical composition of precipitation at the beginning, middle, and ending portions of each storm. Since it is extremely difficult to predict the amount of precipitation expected from a given storm, the sequential samples were changed after every 0.20 to 0.25 inch of liquid precipitation. Samples from the other sensor-activated collector were used to represent "normal" NADP/NTN samples.

All precipitation samples were taken to the Water Quality Lab of the Environmental Resources Research Institute at the Pennsylvania State University and analyzed for the following parameters: pH, specific conductance, ammonium-nitrogen, nitrate-nitrogen, chloride, sulfate, calcium, magnesium, sodium and potassium. In addition, the liquid volume of each sample was also measured. Specific analytical techniques and equipment used to make the above analyses are given in Table 1.

Standard laboratory quality control and quality assurance procedures were followed. Split sample analyses were included in these procedures whenever sufficient sample volume was available. In addition, simulated rainwater samples from the U.S. Department of Commerce, National Bureau of Standards were submitted to the lab during sample analysis. The results from both split and reference standard analyses are given in Appendix A. Whenever available, the means of the split sample analyses were used in evaluating the results of this study. In addition to these quality assurance samples, the water quality lab also participates in a number of EPA sponsored QA/QC programs and interlab comparisons, including EPA's Acid Rain Performance Survey. Although the results of these QA/QC audits are not contained in the Appendix, they are available upon request. The Belfort weighing-bucket type recording rain gauges were used to determine both measured and recorded precipitation amounts. Recorded precipitation volumes from the unshielded gauge were used to represent the "normal" NADP/NTN estimate of precipitation. Eight-hundred and twenty-three mL of polyethylene

Table 1. Summary of Analytical Chemical Techniques.

Parameter	Methodology (Reference)	Equipment
pH	EPA Electrometric (150.1)	Orion 901 Ionanalyzer Serial #8001
Specific Conductance	EPA Specific Conductance (120.1)	YSI Conductance Meter Model 32
Sulfate	EPA Ion Chromatography (300.0)	Dionex Ion Chromatography Unit #20101
Chloride	EPA Ion Chromatography (300.0)	Dionex Ion Chromatography Unit #20101
Ammonium Nitrogen	EPA-Phenate Method (350.1)	Technicon Autoanalyzer II
Oxidized Nitrogen	Standard Methods-Cadmium Reduction (353.2)	Technicon Autoanalyzer II
Extractable Metals		Perkin Elmer Atomic Absorption Model 703
Calcium	EPA AA Direct Aspiration (215.1)	
Magnesium	EPA AA Direct Aspiration (242.1)	
Potassium	EPA AA Direct Aspiration (258.1)	
Sodium	EPA AA Direct Aspiration (273.1)	

glycol antifreeze were added to each rain gauge bucket prior to an event. This volume is equivalent to one inch of precipitation. Following a storm, the antifreeze-precipitation mixture was measured and the amount of precipitation determined by subtracting the one inch of antifreeze. This measured volume was compared to the recorded precipitation amount obtained by interpretation of the rain gauge chart. These data were used to evaluate the catch efficiency of the Aerochem Metrics collector and in calculating wet deposition. Volumes from the sequential samples were used to determine precipitation-weighted mean concentrations from the sequential samples.

In addition to the precipitation measurements, wind direction, wind run, snow particle size and type, and air temperature were measured at the site. Meteorological data from a weather station located at the Rock Springs Research Farms located approximately nine miles to the west of the track were used as a back-up to the instruments located at the site.

RESULTS AND DISCUSSION

Because of unusual climatic patterns during the past two winters, precipitation in general and snowfall in particular in central Pennsylvania was well below normal. Consequently, only five precipitation events were sampled for chemical analyses during the winter months of 1988 and 1989. Four of these storms produced sufficient volume to permit the collection of sequential samples, although two of the storms did not produce sufficient volume in each sequential sample to permit complete chemical analysis. The fifth storm stopped after the collection of the first sequential sample and thus represents a composite, event sample. The results of the chemical analyses of the sequential and composite samples are given by date in Tables 2 through 6. Also contained in these tables are volume measurements and data on wind direction and velocities, length of sample exposure and cation/anion ratios. A comparison of the sample volume measurements with precipitation measurements from the shielded and unshielded Belfort rain gauges for the five sequentially sampled storms is given in Table 7. Precipitation measurements from the shielded and unshielded rain gauges for six additional storms are given in Table 8.

Table 2. Precipitation chemistry and volume measurements of sequential and composite samples collected during a snow storm of January 25-26, 1988.

Parameter	Sequential Samples #1	#2	#3	Volume Weighted Mean	Composite Samples Sensor Act.	Manual Act.
Specific Cond, uS/cm	11.5	8.7	13.2	10.45	10.8	10.4
Volume, in	0.13	0.11	0.02	0.26	0.20	0.27
pH	4.59	4.75	4.58	4.66	4.62	4.59
NH_4, mg/L	0.07	0.06	0.12	0.07	0.095	0.090
NO_3, mg/L	1.20	1.28	1.86	1.28	1.37	1.42
Cl, mg/L	0.24	0.06	0.16	0.21	0.19	0.19
SO_4, mg/L	0.43	0.33	0.30	0.38	0.49	0.50
Ca, mg/	0.12	0.14	----	----	0.15	0.14
Mg, mg/L	0.01	<0.01	----	----	0.01	0.01
Na, mg/L	0.06	0.03	----	----	0.05	0.06
K, mg/L	0.01	0.01	----	----	0.01	0.01
Wind Direction	NNE	N	N-NW-W	----	----	----
Wind Speed, mph	Averaged 5.2 with gusts to 22.8 during storm					
Length of Exposure, hr	4.5	5.5	5.0	----	15.0	20.0
Cation/ Anion Ratio	1.121	1.041	---	----	1.060	1.071

Comments: Moderate to heavy snow in beginning of storm. Winds initially from Northeast gradually shifting to the West. Insufficient sample volume to allow for analysis of Ca, Mg, Na, and K for third sequential sample. Wind speed taken from instrument located at Rock Springs research farm approximately nine miles west of the study site.

Table 3. Precipitation chemistry and volume measurements of sequential and composite samples collected during a snow storm of February 11-12, 1988.

Parameter	Sequential Samples #1	#2	#3	Volume Weighted Mean	Composite Samples Sensor Act.	Manual Act.
Specific Cond, uS/cm	8.3	5.5	16.5	8.28	8.7	11.0
Volume, in	0.17	0.09	0.03	0.29	0.28	0.30
pH	4.68	4.85	4.37	4.66	4.76	4.54
NH_4, mg/L	0.075	0.05	0.120	0.072	0.093	0.105
NO_3, mg/L	1.46	0.75	1.55	1.25	1.51	0.64
Cl, mg/L	0.17	0.050	0.21	0.136	0.245	0.165
SO_4, mg/L	0.20	0.22	1.20	0.27	0.49	0.63
Ca, mg/L	0.26	0.03	----	----	0.28	0.10
Mg, mg/L	0.01	<0.01	----	----	0.04	0.015
Na, mg/L	0.08	0.03	----	----	0.155	0.095
K, mg/L	0.01	0.01	----	----	0.03	0.015
Wind Direction	ENE	NE	NNW-W	----	----	----
Average Wind Speed, mph	5.5	1.3	1.5	----	3.2	3.2
Maximum Wind Gusts, mph	7.5	2.0	13.5	----	13.5	13.5
Length of Exposure, hr	2.5	2.5	2.5	----	7.5	17.5
Cation/ Anion Ratio	1.309	1.145	---	----	1.142	1.027

Comments: Moderate to heavy snow in the beginning of storm. Winds from ENE and brisk at start of first sequential sample shifting to the NE and tapering off. Insufficient sample volume in third sequential sample to allow for analysis of Ca, Mg, Na, and K. Composite samples split to allow for duplicate analysis. Concentrations of composite samples are means of the split sample analyses (Analyses of each sample is in Appendix). Wind speed and direction taken on site. Wind gusts from Rock Springs research farm located nine miles west of study site.

Table 4. Precipitation chemistry and volume measurements of sequential samples collected during a snow storm of March 3-4, 1988.

Parameter	Sequential Samples #1	#2	#3	#4	Volume Weighted Mean	Composite Samples Sensor Act.	Manual Act.
Specific Cond, uS/cm	30.5	38.7	27.6	9.4	32.3	30.8	32.4
Vol., in	0.11	0.43	0.26	0.06	0.86	0.85	0.90
pH	4.12	3.99	4.11	4.66	4.09	4.10	4.07
NH_4, mg/L	0.365	0.53	0.21	0.09	0.381	0.47	0.465
NO_3, mg/L	3.41	3.34	2.48	1.09	2.93	2.86	3.03
Cl, mg/L	0.24	0.21	0.10	0.18	0.178	0.135	0.155
SO_4, mg/L	2.08	2.82	2.24	0.29	2.37	2.24	2.39
Ca, mg/L	0.47	0.165	0.16	0.03	0.193	0.195	0.175
Mg, mg/L	0.02	0.01	0.01	<0.01	0.011	0.01	0.01
Na, mg/L	0.09	0.09	0.04	0.03	0.07	0.04	0.035
K, mg/L	0.02	0.14	0.01	0.01	0.078	0.02	0.02
Wind Direction	NE	NE	NE	NE	----	NE	NE
Avg. Wind Speed, mph	1.75	5.25	0.75	0.5	----	2.65	2.65
Max. Wind Gusts, mph	3.0	6.0	3.0	1.5	----	6.0	6.0
Length of Exposure,hr	3.0	10.0	5.5	2.0	----	20.5	27.7
Cation/ Anion Ratio	1.195	1.250	1.118	1.060	1.160	1.225	1.191

Comments: Storm started as rain and changed to mixed rain and snow. Winds from the NE during the entire storm. Composite samples and second sequential sample concentrations represent mean of split samples. Average wind speed and direction measured at study site. Wind gusts measured at Rock Springs research farm located nine miles west of study area.

Table 5. Precipitation chemistry and volume measurements of sequential samples collected during a snow storm of March 5-6, 1989.

Parameter	Sequential Samples #1	#2	#3	Volume Weighted Mean	Composite Samples Sensor Act.	Manual Act.
Specific Cond, uS/cm	8.9	12.7	7.5	9.5	8.8	9.0
Volume, in	0.56	0.14	0.07	0.77	0.63	0.67
pH	4.76	4.65	5.05	4.75	4.79	4.89
NH_4, mg/L	0.005	0.015	0.035	0.0095	<0.005	0.025
NO_3, mg/L	0.66	1.02	1.06	0.77	0.75	1.06
Cl, mg/L	0.10	0.21	0.30	0.138	0.19	0.18
SO_4, mg/L	0.59	0.86	0.29	0.612	0.40	1.83
Ca, mg/L	0.10	0.15	0.32	0.129	0.11	0.36
Mg, mg/L	0.01	0.02	0.02	0.013	0.01	0.02
Na, mg/L	0.03	0.14	0.14	0.06	0.03	0.13
K, mg/L	0.03	0.06	0.03	0.035	0.01	0.01
Wind Direction	E	NE	NE	-----	----	-----
Average Wind Speed, mph	1.9	5.2	8.6	-----	5.2	5.2
Maximum Wind Gusts, mph	13.2	15.7	18.3	-----	18.3	18.3
Time of Exposure, hr	8.0	4.0	2.0	-----	14.0	19.5
Cation/ Anion Ratio	0.988	0.993	1.116	1.011	0.943	0.659

Comments: Storm began as heavy rain from NE which accounted for most of the total precipitation. During mid-portion of storm rain turned to snow. All snow at end of storm. Wind directions measured at site. Wind Velocities from Rock Springs research farm located approximately nine miles west of the study site.

Table 6. Precipitation chemistry and volume measurements of sequential and composite samples collected during a snow storm of March 20-21, 1989.

Parameter	Sequential Sample	Composite Samples: Sensor Activated	Composite Samples: Manual Activated
Specific Cond, uS/cm	16.8	20.5	29.1
Volume, in	0.25	0.26	0.28
pH	4.47	4.39	4.20
NH_4, mg/L	0.13	0.13	0.135
NO_3, mg/L	1.82	1.91	3.01
Cl, mg/L	0.11	0.13	0.17
SO_4, mg/L	0.73	1.01	1.30
Ca, mg/L	0.07	0.08	0.09
Mg, mg/L	0.01	0.01	0.01
Na, mg/L	0.02	0.02	0.03
K, mg/L	0.02	0.01	0.01
Wind Direction	S changing to SW to W to N		
Average Wind Speed, mph	6.4	6.4	6.4
Maximum Wind Gusts, mph	11.5	11.5	11.5
Length of Exposure, hr	11.0	11.0	26.7
Cation/ Anion Ratio	0.983	0.972	0.963

Comments: Majority of snowfall occurred during first part of storm when winds were from the south. Wind velocities were at their highest when from south and diminished as they shifted to the southwest and west and then intensified again when from the north. Precipitation during later stages of storm in the form of flurries. Insufficient volume to collect sequential samples. Consequently, all three samples represent composite samples, two collected using sensor-activated sampler and one from manual-activated sampler. Wind speed and direction measured at study site. Maximum wind gusts measured at Rock Springs research farm located nine miles west of study area.

Table 7. Comparison of precipitation measurements in inches from sequential and composite samplers and shielded and unshielded Belfort weighing-type rain gauges.

Storm Dates/ Form of Precip	Total of All Sequential Samples	Composite Samples		Rain Gauge Shield		
		Sensor Act.	Manual Act.	None	Alter	Nipher
1/25-26/88 100% Snow	0.26	0.20	0.27	0.22	0.31	----
2/11-12/88 100% Snow	0.29	0.28	0.30	0.29	0.31	----
3/03-04/88 20% Snow 80% Rain	0.86	0.85	0.90	0.82	0.89	----
3/05-06/89 75% Rain 25% Snow	0.78	0.63	0.68	0.72	0.89	1.03
3/20-21/89 100% Snow	0.25	0.26	0.28	0.33	0.37	0.39
Efficiency Ratio	0.881	0.801	0.878	0.857	1.0	----

Comments: Volumes of individual sequential samples are given in Tables 2-6. Precipitation measurements were determined from interpretation of rain gauge chart. Information on wind speed and direction is given in Tables 2-6. Efficiency ratio determined as a function of the precipitation measurement from the Alter-shielded rain gauge.

Table 8. Comparison of precipitation measurements from shielded and unshielded Belfort weighing-type rain gauges.

Storm Date/ Form Precip	Shield Type	Precipitation (in) Measured	Precipitation (in) Recorded	Measured Volume as % of other Gauges	Wind Direction Speed,mph Gusts,mph
1/25-26/88	None	0.21	0.22	77.8(A)	NNW
100% snow	Alter	0.27	0.31	128.6(U)	5.2
	Nipher	----	----	----(N)	22.8
2/11-12/88	None	0.28	0.29	96.6(A)	N
100% Snow	Alter	0.29	0.31	103.6(U)	3.2
	Nipher	----	----	----(N)	13.5
3/03-04/88	None	----	0.82	92.1(A)	NE
80% Rain	Alter	----	0.89	108.5(U)	2.6
20% Snow	Nipher	----	----	----(N)	6.0
1/16/89	None	0.30	0.35	93.8(A), 88.2(N)	W
Sleet &	Alter	0.32	0.34	106.7(U), 94.1(N)	4.8
Frz. Rain	Nipher	0.34	0.36	113.3(U),106.3(A)	18.2
2/06/89	None	0.48	0.48	88.9(A), 87.3(N)	N
95% Rain	Alter	0.54	0.54	112.5(U), 98.2(N)	3.4
	Nipher	0.55	0.52	114.6(U),101.9(A)	19.4
2/13-15/89	None	0.88	0.90	93.6(A), 90.7(N)	NNW
75% Rain	Alter	0.94	0.94	106.8(U), 96.9(N)	2.4
25% Ice	Nipher	0.97	0.98	110.2(U),103.2(A)	7.8
2/21/89	None	0.75	0.79	97.4(A), 96.2(N)	WSW
100% Rain	Alter	0.77	0.78	102.7(U), 98.7(N)	4.6
	Nipher	0.78	0.77	104.0(U),101.3(A)	18.0
2/26-3/3/89	None	0.28	0.29	103.7(A),107.7(N)	SSE
55% Rain	Alter	0.27	0.27	96.4(U),103.8(N)	4.9
45% Snow	Nipher	0.22	0.26	92.9(U), 96.3(A)	24.3
3/05-06/89	None	0.68	0.72	77.3(A), 65.4(N)	NE
75% Rain	Alter	0.88	0.89	129.4(U), 84.6(N)	5.2
25% Snow	Nipher	1.04	1.03	152.9(U),118.2(A)	18.3
3/14-20/89	None	0.20	0.18	95.2(A), 83.3(N)	NE
50% Rain	Alter	0.21	0.17	105.0(U), 87.5(N)	4.7
50% Snow	Nipher	0.24	0.15	120.0(U),114.3(A)	29.8
3/20-21/89	None	0.27	0.33	75.0(A), 71.1(N)	WSW
100% Snow	Alter	0.36	0.37	133.3(U), 94.7(N)	6.4
	Nipher	0.38	0.39	140.7(U),105.6(A)	11.5

Comments: Precipitation in bucket measured directly and estimated from raingage chart. None (U), Alter (A), Nipher (N).

Chemical Analyses

pH

Hydrogen ion concentrations (expressed as pH) were quite variable both within and between storms. This variability was sufficient to preclude detection of any definite trend or pattern in precipitation pH, recognizing of course that the number of available data points are quite limited. The differences in pH of sequential samples collected during the individual storms varied from 0.17 to 0.67 pH unit (Tables 2-6).

There is some indication that the amount of variability within a storm may have been related to changes in wind direction during the storm. For example, pH values for the February 11-12, 1988 storm (Table 3) ranged from 4.68 at the beginning of the storm when the wind was out of the East-Northeast to 4.37 at the end of the storm when the wind was predominately from the Northwest or West. A similar pattern was evident during the January 25-26, 1988 (Table 2) and the March 3-4, 1988 (Table 4) storms, although wind direction remained constant during the later storm and shifted from the Northeast to the Northwest during the January 25-26, 1988 storm. Storms that track from West to East in Pennsylvania generally have much lower pH values than those that move into the state from the East Coast. These differences are related to relatively higher sulfur and nitrogen oxide emissions in western than eastern Pennsylvania.

In comparison to the composite samples, the volume-weighted mean pH of the sequential samples were generally lower (more acidic) than the sensor-activated composite samples and generally higher (less acidic) than the manually-activated composite samples. However, the differences between the sequential mean pH values and either the sensor-activated composite samples or the manually-activated composite samples were quite small ranging from 0.01 to 0.10 pH unit and from 0.02 to 0.14 pH unit, respectively. As expected, the pH values from the manually-activated composite samples were more variable (because of inputs from dryfall) when compared to the sequential samples than the sensor-activated composite sample pH values. However, the pH of samples from the manually-activated sampler were generally (4 out of 5 storms) more acidic than the sensor-activated samples. This might suggest that unsampled precipitation (due to sampler response time) during the early and later stages of a storm was influencing the pH of the sensor-activated samples. This is supported by the fact that, for the most part, precipitation was more acidic at the beginning and ending of the storm and that the manually-operated sampler consistently caught more precipitation that the sensor-activated sampler. Why the sequentially sampled means differ from the sensor-activated composite pH values is uncertain.

Ammonium-Nitrogen

No consistent pattern in ammonium concentrations in sequential samples was evident for all storms sampled, although ammonium concentrations varied considerably within storms ranging from 0.03 to 0.44 mg/L (Tables 2-6). Nevertheless, there is some indication that ammonium concentrations were lower at the beginning and middle portions of the storms than at the end of the storms. When snowfall dominated the form of precipitation (Tables 2 and 3), ammonium concentrations were consistently lower during the middle portion of the storm and highest at the end of the storm. Changing wind direction (East, Northeast to West, Southwest) and generally higher ammonium concentrations in western Pennsylvania may have had some influence on this pattern. No consistent pattern was evident for the storms comprised of both rain and snow.

In comparison to composite storm samples, the volume-weighted mean ammonium concentrations of the sequential samples were consistently lower (Tables 2-6). The differences in concentration between the manually-activated composite samples and the sequentially sampled means ranged from 19% to 62% (0.02 to 0.09 mg/L). For the most part, ammonium concentrations from the sensor-activated and manually-activated composite samplers were fairly similar; although some differences were evident, these differences were quite small (generally 0.01 mg/L or less) and did not exhibit any consistent pattern. Consequently, it is difficult to ascertain, given the limited data available, whether unsampled precipitation (due to sensor response time) is affecting ammonium concentrations in sensor-activated collectors. However, given the observed variations in ammonium concentrations during sequentially sampled storms, the possibility does exist that unsampled precipitation could influence the concentration of precipitation collected with sensor-activated Aerochem Metrics collectors.

Nitrate

Differences in nitrate concentrations between sequential samples varied from 0.40 mg/L to 2.32 mg/L. Between storm nitrate concentrations ranged from 0.77 mg/L to 2.93 mg/L based on the volume-weighted means of the sequential samples (Tables 2-6). Because of this variability, specific temporal patterns were difficult to ascertain, although there is some indication that nitrate concentrations were generally lower in the beginning and middle portions of the storms and highest at the end of the storms. Part of this suggested pattern might be explained by variations in wind direction within and between storms. Two of the four storms sequentially sampled experienced their highest nitrate concentrations at the end of the storm. Wind direction for both storms changed from the East or Northeast to the Northwest or West during the course of the storm and were comprised entirely of snow. As previously stated, air masses in the western portion of Pennsylvania tend to be more polluted than

in the eastern portion of the state. The only storm that demonstrated decreasing nitrate concentrations throughout the storm (Table 4) maintained a consistent Northeasterly wind direction. In contrast, nitrate concentrations during the March 5-6, 1989 storm (Table 5) increased throughout the storm as the winds shifted from the East to the Northeast. Such variability might suggest local pollution were sources influencing nitrate concentrations at the site.

Nitrate concentrations from the manually-activated composite samples were consistently higher than either the sensor-activated composite samples or the volume-weighted mean concentrations from the sequential samples (Tables 2-6). This suggests that dryfall during periods of low intensity precipitation or when precipitation ceased temporarily (which should have caused the sensor-activated collectors to close) might be a contributing factor. The differences in nitrate concentrations between the manually-activated samples and the sensor-activated composite samples and the volume-weighted means from the sequential samples ranged from 0.10 mg/L to 0.39 mg/L and from 0.02 mg/L to 0.26 mg/L, respectively. Although no consistent patterns existed between the concentration data for both composite samples and the sequential samples, there is a suggestion that unsampled precipitation due to sensor sensitivity, particularly during snowfall, might influence the nitrate concentrations in samples collected with the standard sensor-activated Aerochem Metrics sampler. This is supported by the fact that precipitation volumes from sensor-activated samplers were generally smaller than those measured in the manually-activated sampler (Table 7).

Sulfate

Differences in sulfate concentrations during the four sequentially sampled winter storms varied from 0.13 mg/L to 1.00 mg/L (Tables 2-6). Temporal variability within and between storms was so great that no temporal pattern was evident. Within storm sulfate concentration variability did not appear to be related to wind direction, or any other climatic parameter measured.

The potential impact of within storm temporal variability is evident when the mean volume-weighted sulfate concentrations from the sequential samples are compared to the composite event samples. The sequential mean sulfate concentrations were from 0.02 mg/L to 1.22 mg/L lower than the manually-activated composite samples. The largest difference might be atypical based on the fact that the manually-activated sampler was exposed for more that 5.5 hours longer than the sensor-activated sampler, because of light flurry activity. The sequentially sampled mean concentrations were lower (0.11 and 0.36 mg/L) than the means from the sensor-activated sampler for two storms, but higher (0.21 and 0.28 mg/L) during the other storms. Sulfate concentrations from the manually-activated samples were consistently greater (0.01 mg/L to 1.13 mg/L) than the sensor-activated composite samples. These differences might

reflect the relative length of time the various samples were exposed to dry deposition. Although unsampled precipitation due to poor sensor response time could possibly affect sulfate concentrations in Aerochem Metrics sampled winter storms, the significance or direction of such impacts could not be determined from the data collected during this study.

Chloride

Chloride concentrations also varied during individual storms. These variations were fairly consistent, with the differences ranging from 0.14 mg/L to 0.20 mg/L. Actual chloride concentrations ranged from 0.10 to 0.30 mg/L (Tables 2-6). Although the concentration data themselves do not indicate any specific pattern, analysis of these data with respect to wind direction and the location of potential sources of chloride does reveal a fairly consistent pattern.

Wind direction during the early stages of both the January 25-26, 1988 and February 11-12, 1988 storms was primarily from the North or Northeast bringing with it sea salt and consequently relatively high chloride concentrations. As the wind shifted during the middle portion of the storm to the relatively chloride-free air mass located to the North of Pennsylvania, chloride concentrations dropped substantially. The higher chloride concentrations during the latter stages of the storms when winds were from the Northwest or West reflect the generally higher chloride concentrations found in western Pennsylvania as a result of the combustion of coal and the release of HCL. The generally decreasing pattern of chloride concentrations during the March 3-4, 1988 storm could reflect, to a great extent, the movement of the storm away from the state and a subsequent decrease in the influence of sea salt in central Pennsylvania. However, this explanation does not explain the increasing pattern evident during the March 5-6, 1989 storm, although subtle differences in the storm track may influence these differences. Unfortunately, complete sodium concentration data were not available for all sequentially sampled storms. Nevertheless, the available sodium data do tend to support the significance of storm track and sea salt influence on chloride concentrations.

No consistent pattern was evident between the volume-weighted mean chloride concentrations from the sequential samples and either the manually-activated or sensor-activated composite samples. Differences in chloride concentrations between the manually-activated samples and the sequential means ranged from 0.02 to 0.04 mg/L with half of the composite samples being greater than the sequential means and vice versa (Tables 2-6). The sensor-activated composite sample concentrations followed an identical pattern, but had generally higher concentrations. Differences in concentrations between the sequential means and the sensor-activated composite samples ranged from 0.02 to 0.11 mg/L. The reasons for this variability and why sequentially sampled means would be greater than manually-activated or sensor-activated composite samples is unclear.

Calcium

Of the four sequentially sampled storms, only two produced sufficient volumes to permit the determination of calcium concentrations for all sequential samples. However, partial analyses are available from two additional storms for at least two of the three sequential samples (Tables 2 and 5). During one storm (March 3-4, 1988; Table 4), calcium concentrations decreased from 0.47 mg/L at the beginning of the storm to 0.03 mg/L at the end of the storm. During another storm (March 5-6, 1989; Table 5), calcium concentrations increased from 0.10 mg/L to 0.32 mg/L as the storm progressed. Wind direction during both storms was from the East or Northeast and did not change very much. A similar pattern was evident for the two storms where only two sequential samples contained sufficient volume for calcium analysis (Tables 2 and 3). Although limited in number, the results do indicate that calcium concentrations vary during winter storms.

Calcium concentrations were measured in five sensor-activated and five manually-activated composite samples of which only two had comparable sequential sample means (Tables 2-6). Although the calcium concentrations from the sensor-activated composite samples agreed fairly well with the two sequential sample means, the calcium concentration in one of the manually-activated composite samples was 0.23 mg/L greater. This higher concentration (March 5-6, 1989) may be a result of analytical error as indicated by the low cation/anion ratio. It may also reflect the influence of dryfall in that the sampler was exposed 5.5 hours longer than either sensor-activated sampler due to light flurry activity. However, the potential influence of dryfall was not evident in the other samples as indicated by the fact that the calcium concentrations from the sensor-activated samples were greater than the manually-activated samples for three of the remaining four storms. The reason for the higher calcium concentrations in sensor-activated samples is unclear.

Magnesium

Magnesium concentrations were measured in five sensor-activated and five manually-activated composite events of which only two had comparable sequentially sampled means (Tables 2-6). In all cases, magnesium concentrations were quite low ranging from less than 0.01 mg/L to 0.02 mg/L (Tables 2-6). Although magnesium concentrations did vary somewhat, the low concentrations, which are typical for central Pennsylvania, and the limited data makes it very difficult to detect any temporal patterns. Unlike some of the other analytes, magnesium concentrations in both composite samples and the sequential means agreed fairly well, partly due to their low concentrations.

Sodium

Sodium concentrations were measured in five composite sensor-activated and manually-activated events of which only two had comparable sequentially sampled means (Tables 2-6). Sodium concentrations in the sequential samples ranged from 0.03 mg/L to 0.14 mg/L and exhibited a temporal pattern similar to chloride concentrations. Sodium concentrations in the composite samples ranged from 0.02 mg/L to 0.155 mg/L. Sequentially sampled event means were higher than both sensor-activated composite sodium concentrations but not for both manually-activated composite samples. The sodium concentration in the March 5-6, 1989 manually-activated composite sample was substantially higher than either the sequential sample mean or the sensor-activated mean. This difference might reflect analytical error as indicated by the previously mentioned low cation/anion ratio.

Potassium

Like magnesium, potassium concentrations were generally very low, seldom exceeding 0.01 mg/L. This was true for sequentially sampled means as well as the composite event samples. The only exception was a 0.14 mg/L concentration measurement in the second sequential sample of the March 3-4, 1988 storm (Table 4). Since potassium concentrations in both composite samples from this storm were 0.02 mg/L, it is likely that the second sequential sample concentration is in error. A relatively high cation/anion ratio (1.225) supports this suspicion.

Water Quantity

Sampler Comparisons

The liquid volume trapped in the sequential sampler and the composite, sensor-activated and manually-activated samplers are compared in Table 7 along with recorded precipitation estimates from the shielded and unshielded rain gauges. In all cases, the manually-activated sampler trapped more precipitation than the sensor-activated sampler. The increased volumes varied from 0.02 inch (7%) to 0.07 inch (35%). When compared to the sequential sampler volumes, the manually-activated composite sample volumes were greater (from 0.01 inch, 4% to 0.04 inch, 4.6%) for all events except the March 5-6, 1989 storm. During this storm the sequential sampler trapped 0.10 inch (15%) more precipitation than the manually-activated sampler. During this and other storms that had fairly strong winds predominately from one direction, snow accumulated in the bucket unevenly with the greatest depth being downwind. When such conditions occurred, snow trapped in the bucket was more likely to be blown out of the composite bucket or was less likely to be trapped in the composite bucket than in the sequential sampler. This was also the reason why the sensor-activated event sampler volume during the March 5-6, 1989 storm was substantially lower (0.15 inch, 19%) than the total from the sequential sampler and most likely the reason for the discrepancy between these samplers during the

January 25-26, 1988 storm. The larger manually-activated sample volumes reflect, for the most part, precipitation that was not sampled by the sensor-activated collectors due to poor sensor response time and the frequent opening and closing of the sampler during low intensity storms. With the exception of the January 25-26, 1988 and March 5-6, 1989 storms (which were discussed above), the sensor-activated composite sample volumes were very comparable to the total volume of all sequential samples. These results suggest that sample volumes from sensor-activated Aerochem Metrics samplers have a tendency to under-sample precipitation (when compared to the manually-activated sampler) and that the magnitude of the loss will be dependent upon the amount and form of precipitation and wind speed and direction.

When compared to recorded precipitation volumes from the unshielded Belfort rain gauge, the total volume of the sequential samples equaled or exceeded the unshielded rain gauge measurements for four of the five storms. The maximum deviation was 0.06 inch. During the March 20-21, 1989 storm, recorded precipitation in the unshielded gauge was 0.08 inch higher than the composited sequential samples. In contrast, the sensor-activated composite volumes were smaller than the unshielded gauge for all but one storm; the maximum difference was 0.09 inch. Manually-operated sampler volumes were greater (by as much as 0.08 inch) than the unshielded rain gauge during three storms and less (by as much as 0.05 inch) during two storms. The underestimation by the manually-operated gauge was most likely due to snow being blown out of the bucket for reasons previously discussed.

With exception of the March 3-4, 1988 storm, the Alter-shielded gauge recorded more precipitation than any of the Aerochem Metrics samplers, as well as the unshielded rain gauge. The volume differences varied from as little as 0.01 inch to as much as 0.26 inch (Table 7). If the Alter-shielded rain gauge precipitation measurement is assumed to be the most accurate measurement of precipitation for these storms and that the chemistry of unsampled precipitation is the same as that sampled, the average wet deposition estimates for the five storms based on the unshielded precipitation gauge measurement would be in error by an average of 14%. If the volume from the sensor-activated Aerochem Metrics sampler is used in place of the precipitation measurement from the unshielded gauge, wet deposition would be underestimated by approximately 20%. Wet deposition estimates from the sequential sampler and the manually-activated composite sampler would be approximately 12% lower.

Shielded and Unshielded Rain Gauge Comparison

Precipitation data from 11 winter storms were evaluated to determine the influence of wind shields on the volume of precipitation recorded by the Belfort weighing-type rain gauge. In addition to the recorded values, direct measurements of precipitation volumes were also determined to evaluate the accuracy of the recording device. The data, which are summarized in Table 8, show clearly that the catch efficiency of the Belfort rain gauge is influenced by wind and wind shield design. On average, the Alter-shielded gauge caught 0.05 inch (11.5%) more precipitation (based on direct measurement) than the unshielded gauge, while the Nipher-shielded gauge caught 0.09 inch (18%) more than the unshielded gauge. Maximum differences in measured precipitation between the unshielded and Alter-shielded and Nipher-shielded gauges were as much as 29% (0.20 inch) and 53% (0.36 inch), respectively, for individual storms. It is obvious from these results that the unshielded Belfort rain gauge underestimates precipitation amounts and that estimates of wet deposition based on unshielded rain gauge measurements could be in error by as much 18% on average and as high as 53% during individual events.

Compounding these errors are additional errors associated with the the accuracy of the rain gauge measurements and the correct interpretation of the rain gauge chart. When compared to the various recording rain gauge estimates, the volumes of precipitation actually measured in the rain gauge buckets were generally less, with the differences ranging from zero to 0.09 inch and averaging 0.024 inch over the sampled storms. Although these differences might be viewed as being relatively small, it should be noted that the Belfort recording rain gauges used in this study were calibrated before and during the study to assure the highest possible accuracy. Belfort gauges used at most NADP/NTN sites are generally calibrated annually or bi-annually and are thus prone to greater potential error in estimating precipitation amounts.

SUMMARY AND CONCLUSIONS

A comparison of sequentially sampled precipitation volumes and chemistry with sensor-activated and manually-activated samplers using the NADP/NTN approved Aerochem Metrics collector was conducted at the Pennsylvania State University in central Pennsylvania. Precipitation measurements from unshielded, Alter-shielded, and Nipher-shielded Belfort recording rain gauges were also compared. The results indicate that the chemistry of winter precipitation events can vary substantially within storms and that the variations may be related to changes in wind direction and emission sources as a storm moves through the area. Precipitation volume estimates based on sensor-activated sequential and composite samplers and manually-operated samplers

indicate that the sensor-activated composite sampler, which was considered to be representative of normal NADP/NTN sampling protocols, undersampled precipitation because of slow response time upon initiation of precipitation and the frequent opening and closing of the roof during periods of low intensity precipitation. Precipitation may also go unsampled as a result of being blown out of the sampling container. This problem was observed to occur during several snow storms and can significantly reduce sample volume. The volume of unsampled precipitation was highly variable and appeared to be related to the form of precipitation and possibly other climatic parameters, such as wind speed and direction.

The net effect of unsampled precipitation on storm chemistry and wet deposition estimates is uncertain, difficult to quantify, and highly dependent upon the relative chemistry of unsampled versus sampled precipitation. It is obvious from the results of this limited study that measurement errors related to the collection efficiency of the Aerochem Metrics sampler and variations in precipitation chemistry during a storm are possible and that these errors can have substantial impact on the estimates of seasonal wet deposition. The magnitude of the errors will also be ion specific.

Underestimation of wet deposition can also occur as a result of inaccurate measurement of precipitation using an unshielded Belfort recording rain gauge. The results from this study indicated that the unshielded rain gauge underestimated precipitation volumes when compared to Alter- and Nipher-shielded gauges and that the differences were greater when compared to the Nipher wind shield. Assuming that precipitation measurements from the Nipher-shielded rain gauge are the most accurate and that the chemistry of unsampled and sampled precipitation is the same, wet deposition from the storms sampled would be underestimated by 18% on average and by as much as 53% during individual storms using current NADP/NTN sampling protocols.

Compounding these errors are additional sources of error associated with the accuracy of the Belfort rain gauge. A comparison of recorded precipitation with measured precipitation in the Belfort bucket indicated that the Belfort rain gauge generally overestimated precipitation amounts, although some storms were underestimated. The errors associated with rain gauge accuracy approached 25% on an individual storm basis.

Although the results of this study indicate that intra-storm variability in precipitation chemistry and the sampling efficiency of the Aerochem Metrics collector can affect wet deposition estimates, the limited number of sampled storms and the high degree of variability between and within these storms make it very difficult to quantify the magnitude, direction, and significance of these problems. Nevertheless, the results do suggest that substantial error is possible. Consequently, additional studies need to be undertaken that would provide a greater number of observations.

The results from the shielded and unshielded rain gauge comparisons do indicate that wet deposition based on precipitation measurements from the unshielded Belfort rain gauge are likely to be substantially underestimated. Although these results are similar to other published wind shield comparison studies, additional investigations into the importance of these impacts on wet deposition estimates in various climatic regions need to be undertaken. In addition, a study should be conducted where precipitation chemistry is determined from sequential and composite samples from shielded and unshielded Aerochem Metrics samplers and compared to samples collected with standard NADP/NTN sampling protocols. Such a study should be conducted under a variety of climatic conditions. The accuracy of the NADP/NTN Belfort rain gauge and the effects of aging on the spring balance mechanism also needs to be addressed. All of the above studies are essential to the correct interpretation of spatial and temporal variability of wet atmospheric deposition as determined from precipitation samples collected at NADP/NTN monitoring sites.

APPENDIX

Table 1. Chemical analyses of split precipitation samples.

Parameter	2/11-12/88 Sensor Activated #1	2/11-12/88 Sensor Activated #2	2/11-12/88 Manually Activated #1	2/11-12/88 Manually Activated #2	3/5-6/88 Sequential #2 #1	3/5-6/88 Sequential #2 #2	3/5-6/88 Sensor Activated #1	3/5-6/88 Sensor Activated #2	3/5-6/88 Manually Activated #1	3/5-6/88 Manually Activated #2
Specific Cond., µS/cm	8.7	8.7	10.8	11.2	39.4	38.0	30.8	30.7	32.0	32.7
pH	4.76	4.76	4.54	4.54	3.97	4.01	4.10	4.10	4.07	4.06
NH_4, mg/L	0.095	0.090	0.105	0.105	0.540	0.520	0.48	0.46	0.47	0.47
NO_3, mg/L	1.55	1.46	1.55	1.73	3.37	3.32	2.88	2.84	3.06	3.01
Cl, mg/L	0.25	0.24	0.16	0.17	0.20	0.22	0.14	0.13	0.14	0.17
SO_4, mg/L	0.48	0.50	0.64	0.62	2.78	2.86	2.22	2.26	2.34	2.44
Ca, mg/L	0.26	0.30	0.11	0.09	0.16	0.17	0.20	0.19	0.17	0.18
Mg, mg/L	0.03	0.05	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01
Na, mg/L	0.16	0.15	0.09	0.10	0.09	0.09	0.04	0.04	0.04	0.03
K, mg/L	0.03	0.03	0.01	0.02	0.14	0.14	0.02	0.02	0.02	0.02

Table 2. Chemical analyses of Bureau of Standards Simulated Rainfall.

Parameter	Lab Analyses 1/26/88[a] Sample ID 2694-1	Lab Analyses 1/26/88[a] Sample ID 2694-11	Lab Analyses 3/7/88[b] Sample ID 2694-1	Lab Analyses 3/7/88[b] Sample ID 2694-11	Expected Concentration Sample ID 2694-1	Expected Concentration Sample ID 2694-11
Specific Cond., µS/cm	18.3	96.7	19.9	92.9	26±2	130±2
pH	4.27	3.58	4.26	3.58	4.27±0.03	3.59±0.02
NH_4, mg/L	0.020	0.790	0.010	0.760	----[c]	(1.0)[d]
NO_3, mg/L	0.40	7.00	0.13	6.20	----[c]	7.06±0.15
Cl, mg/L	0.26	0.95	0.24	0.96	(0.24)[d]	(1.0)[d]
SO_4, mg/L	2.53	10.06	2.39	10.19	2.75±0.05	10.9±0.2
Ca, mg/L	0.29	0.09	0.08	0.08	0.14±0.003	0.049±0.011
Mg, mg/L	0.02	0.05	0.03	0.05	0.024±0.002	0.051±0.003
Na, mg/L	0.24	0.43	0.22	0.41	0.205±0.009	0.419±0.015
K, mg/L	0.11	0.17	0.05	0.11	0.052±0.007	0.106±0.008

[a] Sample analyses conducted within one month of expiration date.
[b] Expiration date at time of analyses had passed.
[c] Sample concentration not certified because of instability.
[d] Sample concentration in parentheses also not certified.

U. S. Department of Commerce
Malcolm Baldrige
Secretary

National Bureau of Standards
Ernest Ambler, Director

National Bureau of Standards Certificate of Analysis

Standard Reference Material 2694

Simulated Rainwater

This Standard Reference Material (SRM) has been developed to aid in the analysis of acidic rainwater by providing homogeneous materials as control standards at each of two levels of acidity. SRM 2694 consists of four 50 mL solutions, two at each level, in polyethylene bottles. It was prepared by the dissolution of high-purity salts and acids in high-purity distilled/deionized water. Certified values and method(s) used for certification are given in Table 1. Values in parentheses are *not* certified, but are included for information only. Transition and heavy metals are not included in SRM 2694 as they are not stable in solutions at this pH level. Analysts are referred to SRM 1643b "Trace Elements in Water" for applications involving trace metal determinations.

Table 1

Simulated Rainwater

Constituent Elements/ Parameters	Methods	2694-I	2694-II
pH @ 25 °C	c	4.27 ±0.03	3.59 ±0.02
Specific Conductance (μS/cm @ 25.0°C)	b	26 ±2	130 ±2
Acidity, meq/L	d	0.050 ± 0.002	0.284 ± 0.005
Fluoride, mg/L	a,c	0.054 ± 0.002	0.098 ± 0.007
Chloride, mg/L	a,c	(0.24)	(1.0)
Nitrate, mg/L	a,f	———	7.06 ±0.15
Sulfate, mg/L	a,e	2.75 ±0.05	10.9 ± .2
Sodium, mg/L	a,g,h	0.205 ± 0.009	0.419 ± 0.015
Potassium, mg/L	a,g,h	0.052 ± 0.007	0.106 ± 0.008
Ammonium, mg/L	a,c	———	(1.0) .
Calcium, mg/L	g,i,k	0.014 ± 0.003	0.049 ± 0.011
Magnesium, mg/L	g,j	0.024 ± 0.002	0.051 ± 0.003

The certified values are based on proven reliable methods of analysis. The estimated uncertainties are 2 standard deviations of the certified values, except for uncertainties associated with SO_4, acidity, pH, and specific conductance which are based on scientific judgment and are roughly equivalent to 2 standard deviations of the certified value.

Note: The nitrate value for 2694-I is not certified because of instability. It is believed that bacterial or fungal activity contributes to that instability.

Techniques:

a. Ion Chromatography
b. Conductimetry
c. Potentiometry/Ion Selective Electrodes
d. Coulometry
e. Isotope Dilution Thermal Ionization Mass Spectrometry
f. Spectrophotometry
g. Laser Enhanced Ionization Spectrometry
h. Flame Emission Spectrometry
i. Inductively Coupled Plasma Spectrometry
j. Flame Atomic Absorption Spectrometry
k. Direct Current Plasma Spectrometry

The overall direction and coordination of the technical measurements leading to this certificate were performed under the direction of J.R. DeVoe, Chief, NBS Inorganic Analytical Research Division.

The technical and support aspects involved in the preparation, analysis, and issuance of this Standard Reference Material were coordinated through the Office of Standard Reference Materials by T.E. Gills and L.J. Powell.

Gaithersburg, MD 20899
April 23, 1986
(Revision of Certificate dated 9-19-85)

Stanley D. Rasberry, Chief
Office of Standard Reference Materials

(Over)

The preparation and analyses of these solutions were performed by W.F. Koch, G. Marinenko, T.C. Rains, R.W. Burke, M. Knoerdel, W.R. Kelly, G.C. Turk, Mo De-Ming, M.S. Epstein, T.A. Rush, T.A. Butler, K. Han and M.V. Smith in the NBS Inorganic Analytical Research Division.

The statistical analysis of the certification data was performed by R.C. Paule of the National Measurement Laboratory.

Notice and Warnings to Users:

Expiration of Certification: The data included in this Certificate of Analysis are valid for 6 months from the shipping date.

Precautions: The solutions of SRM 2694 are very dilute, unbuffered, and as such are very susceptible to contamination. Therefore, the solutions should be used immediately upon opening. No assurances can be made as to the composition or stability of the solutions after being opened and recapped. SRM 2694 should be stored in an area free from acid and/or ammonia fumes or vapors. Refrigeration of the solutions is not necessary; however, they should not be exposed to extreme heat.

Additional Information: If conductance and pH are to be measured on the same sample, then conductance must be measured first to prevent leakage from the pH reference electrode filling solution from affecting the conductance. The measurement of pH should be performed according to the guidelines set forth in the attachment to this document to minimize the bias caused by residual liquid junction potentials. Acidimetric titrations should be performed on samples that have been purged of dissolved carbon dioxide to prevent drifting endpoints and high results. Care must be exercised in the determination of chloride and fluoride by ion chromatography to avoid possible errors associated with the negative water-dip in the baseline.

Ammonium ion is not certified in these solutions because of the instability of ammonium ion, particularly in 2694-I. The concentration of ammonium ion in 2694-I was originally 0.1 μg/L, but is gradually decreasing. Thus no value is given for ammonium in this solution. The concentration of ammonium in 2694-II appears to be more stable than in 2694-I. Thus a value of 1.0 mg/L is given *for information only*. However the user should be aware of the possible unreliability of this value. The cause of the instability is not known at this time. It does not appear to affect significantly any other component in the solutions.

The temperature coefficient for the specific conductance of both solutions in SRM 2694 has been determined experimentally to be 1.5 percent per degree Celsius at 25 °C. The density of the solutions is 0.997 g/mL at 23 °C.